

DUSEL Facility Cooling Water Scaling Issues

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DUSEL Facility Cooling Water Scaling Issues

Research Memo for Sally Bahowick For questions contact Bill Daily

Scaling information

Precipitation (crystal growth) in supersaturated solutions is governed by both kenetic and thermodynamic processes. This is an important and evolving filed of research, especially for the petroleum industry. There are several types of precipitates including sulfate compounds (ie. barium sulfate) and calcium compounds (ie. calcium carbonate). The chemical makeup of the mine water has relatively large concentrations of sulfate as compared to calcium, so we may expect that sulfate type reactions.

The kinetics of calcium sulfate dihydrate (CaSO4•2H20, gypsum) scale formation on heat exchanger surfaces from aqueous solutions has been studied by a highly reproducible technique. It has been found that gypsum scale formation takes place directly on the surface of the heat exchanger without any bulk or spontaneous precipitation in the reaction cell. The kinetic data also indicate that the rate of scale formation is a function of surface area and the metallurgy of the heat exchanger. As we don't have detailed information about the heat exchanger, we can only infer that this will be an issue for us.

Supersaturations of various compounds are affected differently by temperature, pressure and pH. Pressure has only a slight affect on the solubility, whereas temperature is a much more sensitive parameter (Figure 1). The affect of temperature is reversed for calcium carbonate and barium sulfate solubilities. As temperature increases, barium sulfate solubility concentrations increase and scaling decreases. For calcium carbonate, the scaling tendencies increase with increasing temperature. This is all relative, as the temperatures and pressures of the referenced experiments range from 122 to 356 °F. Their pressures range from 200 to 4000 psi.² Because the cooling water system isn't likely to see pressures above 200 psi, it's unclear if this pressure/scaling relationship will be significant or even apparent.

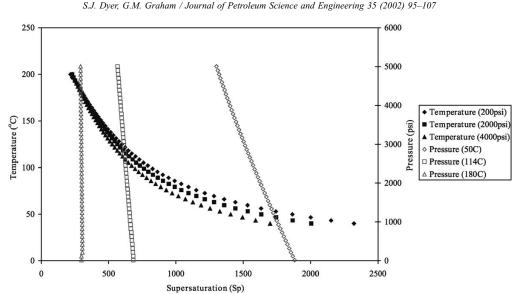


Figure. 1. Predicted barium sulphate supersaturation for the high sulphate scaling brine. Shaded symbols represent the variation in supersaturation with changing temperature at the fixed pressure stated and open symbols represent the variation in supersaturation with changing pressure at the fixed temperature stated.

¹ Z. AMJAD, BFGoodrich Chemical Company, <u>Calcium Sulfate Dihydrate (Gypsum) Scale Formation on Heat Exchanger Surfaces: The Influence of Scale</u>
² S.J. Dyer, G.M. Graham, Oilfield Scale Research Group, Department of Petroleum Engineering, Heriot-Watt University, Riccarton, Edinburgh, UK, <u>The effect of temperature</u> and pressure on oilfield scale formation, Journal of Petroleum Science and Engineering 35 (2002) 95–107

The most common scale minerals found in the oilfield include calcium carbonates (CaCO3, mainly calcite) and alkaline-earth metal sulfates (barite BaSO4, celestite SrSO4, anhydrite CaSO4, hemihydrate CaSO4 1/2H2O, and gypsum CaSO4 2H2O or calcium sulfate). The cause of scaling can be difficult to identify in real oil and gas wells. However, pressure and temperature changes during the flow of fluids are primary reasons for the formation of carbonate scales, because the escape of CO2 and/or H2S gases out of the brine solution, as pressure is lowered, tends to elevate the pH of the brine and result in super-saturation with respect to carbonates. Concerning sulfate scales, the common cause is commingling of different sources of brines either due to breakthrough of injected incompatible waters or mixing of two different brines from different zones of the reservoir formation. A decrease in temperature tends to cause barite to precipitate, opposite of calcite. In addition, pressure drops tend to cause all scale minerals to precipitate due to the pressure dependence of the solubility product.³ And we can expect that there will be a pressure drop across the heat exchanger. Weather or not this will be offset by the rise in pressure remains to be seen. It's typically left to field testing to prove out.

Progress has been made toward the control and treatment of the scale deposits, although most of the reaction mechanisms are still not well understood. Often the most efficient and economic treatment for scale formation is to apply threshold chemical inhibitors. Threshold scale inhibitors are like catalysts and have inhibition efficiency at very low concentrations (commonly less than a few mg/L), far below the stoichiometric concentrations of the crystal lattice ions in solution. There are many chemical classes of inhibitors and even more brands on the market.

System Design Criteria

The proposed system that is subjected to scaling is a water supply to a heat exchanger/chiller (Figure 2). The water source is groundwater at 150 psi in a 6" pipeline. This water is to be "treated" prior to the heat exchanger. The water is assumed to be discharged in the subsurface without any need for further treatment or pressure requirements.

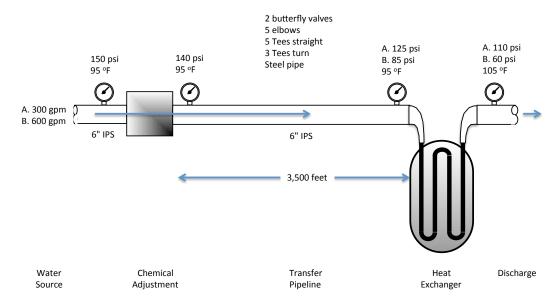


Figure 2. Cooling water treatment supply system

³ He, S.L., Kan, A.T., Tomson, M.B., Rice University; Oddo, J.E., Water Research Institute, <u>A New Interactive Software for Scale Prediction, Control, and Management</u>, SPE Annual Technical Conference and Exhibition, 5-8 October 1997, San Antonio, Texas

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The loss of pressure between the water treatment and the heat exchanger is based on the assumptions listed in Figure 2 and the calculation results detailed in Figure 3.

For pipe section— gate valve— gate valve— ball valve— ball valve— butterfly viv— elbow— tee straight— tee turn— Square inlet— Sum of k values— head loss (ft)—	2 5 5 3	Number of Fittings	or pipe section= gate valve= globe valve= ball valve= check valve= butterfly viv= elbow= tee straight= tee turn= Square inlet= um of k values= head loss (ft)=	
Friction Losses		Frictio	n Losses	
Pipe Section:	Treat to HE		Pipe Section:	Treat to HE
Pipe ID (in):	5.7		Pipe ID (in):	5.7
Pipe Length (ft):		Pi	pe Length (ft):	3500
Flow Rate (gpm):	300	Flo	w Rate (gpm):	600
Roughness (e):		F	Roughness (e):	0.00015
Pipe X-Area (in ²):	25.50	Pig	oe X-Area (in ²):	25.50
Hydraulic Diameter (Dh, ft):	0.48	Hydraulic Dia	meter (D _h , ft):	0.48
Hydraulic Radius (R _h , ft):	0.12	Hydraulic F	Radius (R _h , ft):	0.12
viscosity, v (ft ² /sec):	1.06E-05	viscosi	ty, v (ft2/sec):	1.06E-05
Fluid velocity (ft/sec):	3.77	Fluid ve	locity (ft/sec):	7.55
Reynolds number (Re):	169,122	Reynolds	number (Re):	338,243
e/D:	3.16E-04		e/D:	3.16E-04
Flow type:	Tubulent Flow		Flow type:	Tubulent Flow
Laminar f=			Laminar f=	0.000189
Choosen Friction Factor:		Choosen	Friction Factor:	0.0169
Colebrook Friction Factor (f):	0.0182		ction Factor (f):	0.0169
Itterate f to get "1" here>			get "1" here>	0.9994
Haaland Friction Factor (f)		Haaland Frid	ction Factor (f):	
Swamee-Jain Friction Factor (f)			Friction Factor (f)	
Head loss (ft)=			Head loss (ft)=	109.9779
Head loss (psi)=	12.79		lead loss (psi)=	47.66
Total Head Loss / section	22.2	Total Head Lo		1040
feet			feet	124.9
Head loss (psi)=	14.41	H	lead loss (psi)=	54.12

Figure 3. Pressure ("head") loss calculation results for the 3500' 6"dia pipeline.

There are two water chemistries and two flow rates (300 and 600 gpm) being considered. The resulting four scenarios are presented in Figure 4.

Scenario 1			Scenario 2			Scenario 3			Scenario 4		
Parameter	Value	Units	Parameter	Value	Units	Parameter	Value	Units	Parameter	Value	Units
low Rate	300	gpm	Flow Rate	300	gpm	Flow Rate	600	gpm	Flow Rate	600	gpm
Source Pressure	150	psi	Source Pressure	150	psi	Source Pressure	150	psi	Source Pressure	150	psi
Heat Exchanger:			Heat Exchanger:			Heat Exchanger:			Heat Exchanger:		
Inlet Pressure	125	psi	Inlet Pressure	125	psi	Inlet Pressure	85	psi	Inlet Pressure	85	psi
Outlet Pressure	110	psi	Outlet Pressure	110	psi	Outlet Pressure	60	psi	Outlet Pressure	60	psi
Inlet Temp.	95	°F	Inlet Temp.	95	°F	Inlet Temp.	95	°F	Inlet Temp.	95	°F
Outlet Temp.	105	°F	Outlet Temp.	105	°F	Outlet Temp.	105	°F	Outlet Temp.	105	°F
ЭН	6.82		рН	8.14		рН	6.82		рН	8.14	
Conductivity	5770	μmhos/cm	Conductivity	-	μmhos/cm	Conductivity	5770	μmhos/cm	Conductivity	-	μmhos/cr
TDS	6130	mg/L	TDS	3810	mg/L	TDS	6130	mg/L	TDS	3810	mg/L
rss	43.8	mg/L	TSS	5.6	mg/L	TSS	43.8	mg/L	TSS	5.6	mg/L
Hardness	3850	mg/L	Hardness	1800	mg/L	Hardness	3850	mg/L	Hardness	1800	mg/L
Non-Metals			Non-Metals			Non-Metals			Non-Metals		
Alkalinity	160	mg/L	Alkalinity	-	mg/L	Alkalinity	160	mg/L	Alkalinity	-	mg/L
Bicarbonate	195	mg/L	Bicarbonate	195	mg/L	Bicarbonate	195	mg/L	Bicarbonate	195	mg/L
Carbonate	0	mg/L	Carbonate	-	mg/L	Carbonate	0	mg/L	Carbonate	-	mg/L
Chloride (Cl-)	23	mg/L	Chloride (CI-)	23	mg/L	Chloride (Cl-)	23	mg/L	Chloride (Cl-)	23	mg/L
Cyanide, Total	<10	μg/L	Cyanide, Total	-	μg/L	Cyanide, Total	<10	μg/L	Cyanide, Total	-	μg/L
Cyanide, WAD	<10	μg/L	Cyanide, WAD	<10	μg/L	Cyanide, WAD	<10	μg/L	Cyanide, WAD	<10	μg/L
luoride	1.01	mg/L	Fluoride	1.01	mg/L	Fluoride	1.01	mg/L	Fluoride	1.01	mg/L
Nitrogen, NH4	3.59	mg/L	Nitrogen, NH4	0.745	mg/L	Nitrogen, NH4	3.59	mg/L	Nitrogen, NH4	0.745	mg/L
Nitrogen, NO3	≤0.05	mg/L	Nitrogen, NO3	0.556	mg/L	Nitrogen, NO3	≤0.05	mg/L	Nitrogen, NO3	0.556	mg/L
Nitrogen, NO2	≤0.05	mg/L	Nitrogen, NO2	-	mg/L	Nitrogen, NO2	≤0.05	mg/L	Nitrogen, NO2	-	mg/L
Sulfate (SO4)	4160	mg/L	Sulfate (SO4)	2430	mg/L	Sulfate (SO4)	4160	mg/L	Sulfate (SO4)	2430	mg/L
Dissolved Metals			Dissolved Metals			Dissolved Metals			Dissolved Metals		
Calcium	456	mg/L	Calcium	235	mg/L	Calcium	456	mg/L	Calcium	235	mg/L
Magnesium	658	mg/L	Magnesium	295	mg/L	Magnesium	658	mg/L	Magnesium	295	mg/L
Potassium	62.4	mg/L	Potassium	47.7	mg/L	Potassium	62.4	mg/L	Potassium	47.7	mg/L
Sodium	256	mg/L	Sodium	263	mg/L	Sodium	256	mg/L	Sodium	263	mg/L
/letals, Total			Metals, Total			Metals, Total			Metals, Total		
luminum	19.7	μg/L	Aluminum	24.1	μg/L	Aluminum	19.7	μg/L	Aluminum	24.1	μg/L
Arsenic	238	μg/L	Arsenic	113	μg/L	Arsenic	238	μg/L	Arsenic	113	μg/L
Cadmium	< 1.0	μg/L	Cadmium	-	μg/L	Cadmium	< 1.0	μg/L	Cadmium	-	μg/L
Chromium	< 1.0	μg/L	Chromium	-	μg/L	Chromium	< 1.0	μg/L	Chromium	-	μg/L
Copper	< 5.0	μg/L	Copper	7.74	μg/L	Copper	< 5.0	μg/L	Copper	7.74	μg/L
ron	24500	μg/L	Iron	3180	μg/L	Iron	24500	μg/L	Iron	3180	μg/L
ead	1.27	μg/L	Lead	< 1.0	μg/L	Lead	1.27	μg/L	Lead	< 1.0	μg/L
Manganese .	4280	μg/L	Manganese	623	μg/L	Manganese	4280	μg/L	Manganese	623	μg/L
Mercury	<0.0002	μg/L	Mercury	-	μg/L	Mercury	<0.0002	μg/L	Mercury	-	μg/L
Nickel	< 5.0	μg/L	Nickel	5.83	μg/L	Nickel	< 5.0	μg/L	Nickel	5.83	μg/L
Selenium	< 5.0	μg/L	Selenium	-	μg/L	Selenium	< 5.0	μg/L	Selenium	-	μg/L
Silver	9.2	μg/L	Silver	-	μg/L	Silver	9.2	μg/L	Silver	-	μg/L
Zink	136	μg/L	Zink	51.8	μg/L	Zink	136	μg/L	Zink	51.8	μg/L
Data Source	Water, Bo	ttle #3	Data Source	4100		Data Source	Nater, Bo	ottle #3	Data Source	4100	

Figure 4. Cooling water treatment scenarios.

It is anticipated that any equipment used to support this facility will be rated for heavy industrial use with minimal maintenance requirements and the potential for remote monitoring. It is unknown, but anticipated, that the chiller/heat exchanger may require pre-filtration of the cooling medium.

Belsperse Injection Estimation

Belsperse® 161 is a phosphorus-containing dispersant made up of phosphinopolyacrylates, or an acrylic acid polymer (additional information attached). It is felt that Belsperse 161 is a good calcium carbonate and calcium sulfate dispersant. It is especially effective under high stress and high temperature conditions.⁴

⁴ Robert R. Cavano. "Polymers for cooling water treatment", Water Matters, Scranton Associates, Inc., Part II, Copolymers Analyst, pp 1-14, Winter 2001.

The Environmental Restoration Division at LLNL has been using Belsperse 161 for several years based on experiments done with air stripping equipment⁵. They found that Belsperse was much more effective for reducing scale buildup than the JP-7 polyphosphate formulation (Jaeger Products, Inc.). Their injection procedures call for feed rates initially based on stoichiometry, and adjusted according to field observations.

Estimations of Belsperse 161 injection concentrations, based on stoichiometric relationships, account for pH, temperature, ion-species and inorganics. A spreadsheet calculator, developed by Tom Wolfe of Perlorica Inc.⁶ was used to obtain the required injection concentration for the various conditions anticipated by the design of the mine water cooling stream. A sample input page is shown as (Figure 5). Some critical analytical data, not provided in the scenario 2 and 4 data sets, were supplemented with values from Scenario 1 and 3 including Bicarbonate, Chloride and Flouride.

Based on Scenario 1, with temperatures reaching $140^{\circ}F$ in the heat exchanger, the required Belsperse 161 concentration should be 0.63 mg/L. For the flow rate of 300 gpm this would require an injection rate of 1.3 ml/min of 50% belsperse solution. The concentrations and flow rates for the other scenarios are listed in Table 1. It's likely that higher flow rates would be imposed to account for variations in water chemistry.

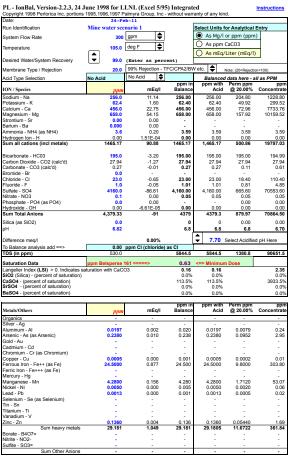


Figure 5. Belsperse 161 calculation input page for Scenario 1.

⁵ P. W. Krauter, "Test of a Chemical Dispersant for the Control of Scale Formation at Treatment Facility D", May 1998, UCRL-ID-130568

⁶ PL - IonBal, Versio

n-2.2.3, 24 June 1998 for LLNL (Excel 5/95), Copyright 1998 Perlorica Inc, portions 1995,1996,1997 Palmyra Group, Inc

Table 1. Belsperse injection calculation results for all scenarios.

	Scenario					
Treatment Parameters	1	2	3	4		
Process flow rate (gpm)	300	300	600	600		
Process temperature (°F)	105	105	105	105		
Belsperse 161 concentration (mg/L)	0.63	2.2	0.63	2.2		
Belsperse 161 injection rate (ml/min)	1.3	4.5	2.6	9		
Belsperse solution usage (gal/day)	0.5	1.8	1	3.6		

Preliminary Treatment System Design

A chemical injection system to support the facility described above should include the following:

- A. Chemical holding/mixing tanks.
- B. Delivery/metering pump
- C. Injection hardware

The chemical holding tanks could be lined drums, polyethylene tanks or FRP vessels. These vessels should not be open to the atmosphere. Very clean water should be used to dilute the Belsperse 161. Non-diluted Belsperse is very viscous and can be problematic to pump and meter as it tends to crystalize easily.

The metering pump should have self calibration or an intrinsic calibration system. The pump could be a diaphragm pump similar to the LMI series pumps (Figure 6). The pumps should be rated to allow injection pulses no less frequent than once per 2 seconds. Remote metering and adjustment are possible with these pumps.



Figure 6. Typical LMI metering pump.

The flow from the "treatment" system to the heat exchanger has a Reynolds number varying from 1.7E5 to 3.4E5. This is neither turbulent nor laminar, but in the "transition" zone. Although the length of the pipeline is significant, it may not be prudent to count on sufficient mixing within this section. It is recommended that a pre-mixer be used to facilitate more thorough mixing (Figure 7). This would include a side stream injection line with a static mixer that would re-enter the main line through an injection probe. This would also facilitate easier maintenance with isolation valves on either end of the pipeline.



Figure 7. Static mixer and injection probe.

All of the appropriate leak detection, check valves and monitoring devices should be employed to ensure that the injection system isn't a weak link in the chain for leaks. A rough layout for an injection system is given as Figure 8.

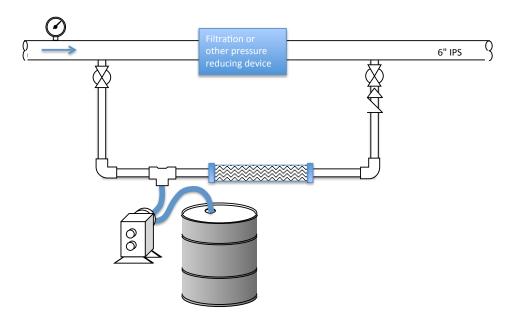


Figure. 8 Diagram of potential injection system.

Conclusions

Based on the water chemistry it is anticipated that there is a high likelihood for sulfate compound precipitation and scaling. This may be dependent on the temperature and pressure, which vary throughout the system. Therefore, various types and amounts of scaling may occur at different locations. Although it has been shown that decreased pressure causes increased scaling, it is unclear if this condition will have significant affect, as all the pressures are low. Sulfate concentrations predominate, but there is still a chance for calcium carbonate buildup, especially in the heat exchanger where the temperatures are rising.

Additional information is needed to conduct a thorough analysis, but it would appear that a fairly simple injection system would be sufficient to address scaling issues.

It would be advisable to:

- 1. Take additional samples of the water to confirm a tighter range of analytical values for a broader list of analytes.
- 2. Get detailed design information about the chiller/heat exchanger and its effect on the water temperature and pressure drop.

- 3. Consult with an organization, such as Intertek (http://www.intertek.com/oil-and-gas/exploration-and-production/scale/), that has experience with this type of treatment system.
- 4. Do field tests to determine the effectiveness and accuracy of the preliminary design.

Belsperse[®]161 **Dispersant – General Product Information**

Belsperse 161 dispersant has been developed as a highly effective scale control agent and dispersant used primarily in boilers and industrial cleaning.

The active ingredient of Belsperse 161 is a phosphinocarboxvlic acid.

Typical Physical Properties

Appearance Colorless liquid
Odor Slight
Solids content 50% (w/w)
Specific gravity 1.20-1.24
pH (undiluted) 3.5-4.5
Viscosity at 25°C 90-150 cSt

Boiling point range 101-103°C (213-217°F) Freezing point range -1 to -3°C (30-27°F)

Theoretical phosphorus

content (as P) 0.8% (w/w)

Solubility in:

water Miscibleethylene glycol Miscible

methanol Precipitate is formed

46% caustic soda Miscible

pH limitations Does not form insoluble

sodium or potassium salts. It is hydrolytically stable and can be incorporated into concentrated

formulations regardless

of the final pH.

Thermal stability (DSC)

Differential scanning calorimetry has shown that Belsperse 161 is stable up to a temperature of 200°C (392°F).

Chemical reactivity

Belsperse 161 is not affected by chlorine or other oxidising biocides under normal use conditions. Further details on safety and handling are available in the materials safety data sheet on this product.

Logistics

Packaging

Classification non-hazardous for conveyance

non-hazardous for supply HDPE 220l XL-ring Mauser

drum

Height 935 mm Diameter 580 mm Gross weight 544 lb Net weight 525 lb

Regulatory approvals

FDA 21 CFR 173.310 – boiler additives

USDA G5: cooling and retort water

G6: boilers and steamlines – possible

food contact

G7: boilers, steamlines and cooling

systems - no food contact

A1: cleaning compounds; meat/poultry

plants

B2/B2: laundry compounds;

meat/poultry plants

Q1: shell egg cleaning; meat/poultry

plants

Toxicology data

Acute oral LD₅₀ (rats) >5000 mg/kg

Eye irritation (rabbits) Non-irritant (EEC guidelines) Skin irritation (rabbits) Non-irritant (EEC guidelines)

Toxicity to fish:

 $\begin{array}{lll} \bullet & \text{rainbow trout} & 96\text{-hr LC}_{50} > 1000 \text{ mg/l} \\ \bullet & \text{zebra fish} & 96\text{-hr LC}_{50} > 1000 \text{ mg/l} \end{array}$

Ecological data

96-hr LC₅₀ (brown >10000 mg/l

shrimp)

24-hr EC_{50} (daphnia) >320 mg/l 72-hr EC_{50} (algae 130 mg/l

inhibition)

COD 890 mg O₂/g

Biodegradation Not readily biodegradable 20% in 28 days (OECD301E)